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(4) Electroconductive resin composition.

G) An electroconductive resin composition contains (i) 100 parts by weight of thermoplastic resins and/or thermosetting resins and (ii) 15 to 150 parts by weight of (a) carbon black having a DPB oil absorption amount of 400 ml/100 g or more and (b) expanded graphite having an average particle size of 40 μm or more, wherein the expanded graphite content is 40 to 90% by weight of the total amount of the carbon black and the expanded graphite.

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#### Description

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#### **ELECTROCONDUCTIVE RESIN COMPOSITION**

#### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

The present invention relates to an electroconductive resin composition exhibiting a high and stable electroconductivity at a small filled amount by using a specific carbon black and graphite in combination as the electroconductive filler in a thermoplastic resin and/or a thermosetting resin.

### 2. Description of the Related Art

Remarkable developments have and are occurring in the field of electronic machines such as computers, VTR, acoustic instruments, home appliances, word processors, etc. In these electronic instruments, due to a high integration density of electronic circuits and devices thereof, microcurrents are used, and thus a problem arises in that an erroneous actuation, etc., may be caused by electromagnetic waves from an external source.

Plastic moldings are frequently used for the casings of these electronic instruments to cope with demands for a lightweight, low cost, mass-produced article, etc., but these plastic moldings have no shielding effect against electromagnetic waves, and thus cannot solve the above problem.

In the prior art, as a method for imparting an electromagnetic wave shielding property to plastic moldings, an electroconductive resin has been proposed comprising an electroconductive filler filled and dispersed in a resin. As the electroconductive filler, a metal type filler and a carbon type filler are generally employed.

A metal type filler is suitable for imparting a high electroconductivity, but has a drawback in that the specific gravity thereof is high, that the electroconductivity is reduced due to filler cutting losses during molding, and that it causes abrasion of the extrusion screws and molds.

A carbon type filler such as carbon black or graphite will not substantially abrade extrusion screws or molds, but it is not suitable for uses for which a high electroconductivity with a volume resistivity value of 1  $\Omega$  cm or less is required, such as electromagnetic shielding materials, electrodes, etc. Among electroconductive carbon blacks, a small amount of Ketjen Black EC (produced by Ketjen Black International) can provide a satisfactory electroconductivity, but the mechanical strength of the composition is remarkably worsened and the resultant material is very brittle and easily destroyed. Graphile itself has a good electroconductivity, but when dispersed in a resin, a high electroconductivity can not be obtained unless a large amount thereof is filled, and further, a problem arises in that the resistance value has a great amplitude of 10 $^{1}$  to 10 $^{-1}$   $\Omega$  cm, and a stable electroconductivity cannot be obtained (Japanese Unexamined Patent Publication (Kokai) No. 60-118744). Further, when carbon black and graphite are used in combination, although a high electroconductivity can be obtained from a low filling amount, the mechanical strength of the composition is lowered and the moldability reduced. Therefore, when a highly electroconductive resin composition is obtained by using the carbon black and graphite of the prior art, molding becomes difficult and the resin composition obtained has a lowered mechanical strength, particularly impact strength, and since carbon black and graphite are more expensive and have a higher specific gravity than the resin, a composition obtained by using these fillers is disadvantageously both high cost and heavy. To improve the moldability, a method has been proposed in which a propylene-ethylene copolymer with a high binder efficiency is formulated (Japanese Unexamined Patent Publication (Kokai) No. 51-17937), and a method in which a resin-coated carbon black and a resin-coated graphite are employed (Japanese Unexamined Patent Publication (Kokai) No. 61-218648), etc., but these methods do not provide a reduction of the filling amount of carbon black and graphite, and thus did not provide a solution to the above problems. Accordingly, desirably a carbon black and graphite capable of exhibiting a high electroconductivity even at a low filling amount should be produced.

### SUMMARY OF THE INVENTION

Accordingly, the objects of the present invention are to eliminate the above-mentioned disadvantages of the prior art and to provide an electroconductive resin composition having a stable and high electroconductivity when a small amount of an electroconductive filler is formulated therein, and an excellent mechanical strength, kneadability, and moldability.

Other objects and advantages of the present invention will be apparent from the following description. In accordance with the present invention, there is provided an electroconductive resin composition comprising (i) 100 parts by weight of at least one resin selected from the group consisting of thermoplastic resins and thermosetting resins and (ii) 15 to 150 parts by weight of (a) carbon black having a DBP oil absorption amount of 400 ml/100 g or more and (b) expanded graphite having an average particle size of 40 µm or more, wherein the expanded graphite content is 40 to 90% by weight of the total amount of the carbon black and the expanded graphite.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present inventors previously proposed a composition having a high electroconductivity even at a filling amount of about 80%, compared with a carbon black of the prior art, for example, Ketjen Black EC (DBP oil absorption amount: 325 ml/100 g) by using a specific carbon black with a DBP oil absorption amount of 400 ml/100 g or more (Japanese Unexamined Patent Publication (Kokai) No. 60-8335). As a result of further investigations, by using a special graphite in combination with the special carbon black, an electroconductive resin composition was obtained which had a high electroconductivity at a filling amount of about 60%, compared with the carbon black and graphite of the prior art, and consequently having a lower cost and improved specific gravity, and having an excellent kneadability and mechanical strength, to accomplish the present invention.

The carbon black usable in the present invention has a DBP oil absorption amount of 400 ml/100 g or more. When the oil absorption amount is smaller, a larger amount of carbon black must be formulated to obtain a resin composition with a high electroconductivity, and thus the mechanical strength is impaired.

On the other hand, although the upper limit value of the DBP oil absorption amount is not particularly limited, when this amount is more than 700 ml/100 g, the dispersibility of carbon black into the resin is reduced, and therefore, preferably the DBP oil absorption amount is in the range of 400 to 600 ml/100 g. The term "DBP oil absorption amount" used in the present specification means the oil absorption amount defined according to ASTM D2414-79.

The expanded graphite usable in the present invention can be prepared by treating natural or artificial graphite with, for example, an inorganic acid such as sulfuric acid, nitric acid, etc., to form graphite interlayer compounds, washing the compounds with water followed by dehydration, abruptly heating and expanding the compounds, and compressing the resultant expanded graphite into a sheet or a mass followed by mechanical pulverization by a Henschel mixer, hammer mill, ball mill, etc., to a particle size of 40 µm or more.

The upper limit value of the particle size of the expanded graphite is not particularly limited, but if 5 cm or larger, kneading becomes undesirably difficult, and therefore, in the present invention, the range of the particle size is preferably from 40 to 20,000 µm.

The amounts of carbon black and expanded graphite used in the present invention are 15 to 150 parts by weight, preferably 20 to 130 parts by weight, based on 100 parts by weight of the thermoplastic and/or thermosetting resin. At an amount lower than this, a high conductivity of 1 x 10°  $\Omega$  cm or lower can not be exhibited, and at an amount higher than this, kneading becomes impossible.

The ratio of the carbon black to the graphite to be used in the present invention may be 40 to 90% by weight, preferably 45 to 85% by weight, for the graphite based on 100% by weight of the total amount of the carbon black and the graphite. When the graphite content exceeds 90% by weight, the electroconductivity is lowered, and at a content lower than 40% by weight, although the electroconductivity is good the mechanical strength is lowered, and thus the object of the present invention tends to be difficult to be achieved.

The thermoplastic resins and thermosetting resins usable in the present invention include various kinds known in the art and are not particularly limited. Specific examples may include thermoplastic resins such as low, medium and high density polyethylenes, linear low density polyethylene, polypropylene, ethylene-propylene copolymer, ethylene-vinyl acetate copolymer, ethylene-acrylic acid ester copolymer, acrylonitrile-buta-diene-styrene ternary copolymer, polystyrene, acrylonitrile-styrene copolymer, nitrile rubber, butadiene rubber, styrene-butadiene rubber, ethylene-propylene-diene rubber, silicone rubber, thermoplastic polyure-thane resin, polyamide resin, polyester resin, polycarbonate, polyvinyl chloride, polyacetal resin, polyphenylene sulfite, polyphenylene oxide, etc. Examples of the thermosetting resins may include thermosetting acrylic resins, phenol resins, unsaturated polyester resins, epoxy resins, urethane resins, alkyd resins, etc.

The electroconductive resin composition of the present invention may further contain additives such as antioxidants, heat-resistant stabilizers, lubricants, flame retardants, pigments, plasticizers, cross-linking agents, UV-ray absorbers, reinforcing agents, etc., conventionally used in thermoplastic resins.

The composition of the present invention can be prepared according to any known method, but preferably is molded into pellets by mixing and kneading uniformly in a conventional manner by a suitable blender such as a kneader, Banbury mixer, mixing rolls, pressure kneader, etc., and these pellets molded into a desired product by press molding, extrusion molding, injection molding, sheeting, blow molding, etc.

According to the present invention, a resin composition with a stable and high electroconductivity can be obtained at a low filling amount of carbon black and graphite, and therefore, is highly electroconductive compared with the resin composition of the prior art, and has an excellent mechanical strength and moldability with a lower specific gravity. Accordingly, the electroconductive resin composition of the present invention can be applied to various fields, and can be utilized not only in electromagnetic wave shielding materials, but also, for example, as an electroconductive material for high voltage cables, Ignition cables, plane heat-generating members, plane switches, electrodes, etc., or for applications such as electronic instruments or IC package materials, as a material for molded video discs, and as a permanent antistatic material, etc.

#### Examples

The present invention will now be further illus trated by, but is by no means limited to, the following

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Examples. The electroconductivity in the Examples was evaluated in terms of the volume resistivity value according to the measuring method of SRIS 2301 of the Rubber Society of Japan, the electromagnetic shielding effect was measured by both a TR-4172 and a shielding box produced by Advantest K.K., and the shielding was evaluated at a shielding of 300 MHz in the electrical field. The mechanical strength of the composition was evaluated by the Izod impact strength value obtained by the method of JIS-K-7110, and the specific gravity of the composition was measured according to the method of JIS-K-7112.

#### Example 1

A polypropylene resin (produced by Idemitsu Sekiyu Kagaku, trade name: J-465H), carbon black and/or the various graphites as shown in Table-1 were formulated in the respective predetermined amounts, kneaded by a Laboplastomill at a temperature of 200°C, and then press molded into a plate 15 cm square with a thickness of 2 mm. The volume resistivity value (hereinafter abbreviated as VR) and the shielding effect of the obtained molded product were measured, and the results thereof are as shown in Table 1, in relation to each electroconductive resin composition.

When graphite alone was used (see Experiments No. 14 - 16), even when filled in an amount of 60 parts by weight based on 100 parts by weight of the total amount of the resin and the graphite, the VR and shielding effect were poor, and the amplitude of the measured value was great. Also, even when the graphite of the present invention was used alone, only a VR and shielding effect substantially equal to that obtained when employing a graphite other than that of the present invention were exhibited. On the other hand, as understood from Table 1, when the carbon black and the graphite of the present invention were used in combina tion (see Experiments No. 1 - 8), VR is about 5 X  $10^{-2} \Omega \cdot \text{cm}$  and the shielding effect was good at about 70 dB and stable with little amplitude of the value, thus having a superior shielding effect by about 15 dB and an about 4-fold VR, compared with the use of a carbon black and graphite other than those of the present invention (see Experiments No. 9 - 13), even at the same filling amount.

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Table 1

		-		Pre	Present Invention	wenti	ទ						Comparative	tive			
Experiment No.	No.		2	3	4	5	9	7	8	6	10	#	12	ដ	14	51	16
Electroconductive resin composition (wt.pa	composition (wt.p	arts)									•						
Polypropylene resin		57	57	. 57	57	5.7	27	57	57.	57	27	57	57	57	40	9	40
DBP oil absorption amount 480 ml/100 g carbon black		13	E	13	13	. 81	0	0	0	13	ជ	13	13	0	0	0	0
420 ml/100 g "		<b>0</b>	0	0	0	0	. EI	13	0	0	0	0	0	0	0	0	0
400 ml/100 g "		0	0	0	0	0	0	0	13	0	0	0	0	0	0	0	0
325 ml/100 g "	<b>!</b> *	0	0	0	0	0	0	0	0	0	0	0	0	13	0	0	0
Graphite powder (average particle size) Expanded graphite (2.8 µm)	e particle size) (2.8 µm)		0	0	0	0	<b>o</b> .	0	0	30		. 0	0	0	0	0	0
=	(4.2 µm)	0	0	0	0	0	0		0	0	30	0	. 0	0	0	0	0
=	(40 µm)	30,	0	0	0	0	0	0	0	0	0	0	0	30	09	0	0
<b>2</b> .	(mu 07)	0	30	0	0	0	30	0	0		0	0	0	0	0	09	0
	(mų 003)	0	0	30	0	Φ	0	. 0	0	0	0	0	0		0	0	0
=	(5 mm)	0	0	0	30	0	0	30	30	0	0	0	0		0	0	0
₹	(10 mm)	0	0	0	0	30	. 0	0	0		0	0	0	0	0	0	0
Vein graphite	(40 µm)	0	0	0	0	0	0	0	0	0	0	30	0	0	0	0	09
Artificial graphite	(mr 08)	0	0	0	0	0	0	0	0	0	Θ.	0	30	0	0	0	0

Table 1 (Continued)

			Pre	Present Invention	nventi	ion						Compa	Comparative			•
Experiment No.	1 2 3 4 5 6 7	2	۳	4	2	9	7	· 8	6	10	10 11 12 13 14 15 16	12	E	14	15	16
Volume resistivity value (በ·cm) *2	6.3x 4	۲. 2-0 0-2 د	3.8x	3.7x 10 <sup>-2</sup>	3.8x	5.1x 10 <sup>-2</sup>	4.7x 10 <sup>-2</sup>	4.1x 3.8x 3.7x 3.8x 5.1x 4.7x 5.0x 10 <sup>-2</sup> 10 <sup>-2</sup> 10 <sup>-2</sup> 10 <sup>-2</sup> 10 <sup>-2</sup> 10 <sup>-2</sup>	1.8x 10 <sup>-1</sup>	1.8x 1.4x 10 <sup>-1</sup> 10 <sup>-1</sup>	1.8x 10 <sup>-1</sup>	2.3x 10 <sup>-1</sup>	1.0x 10 <sup>-1</sup>	2.8x 10 <sup>0</sup>	1.9x 10 <sup>0</sup>	3.0x
	$6.7x \ 4.3x \ 3.9x \ 3.9x$ $10^{-2} \ 10^{-2} \ 10^{-2}$	1.3x 10 <sup>-2</sup>	3.9x 10 <sup>-2</sup>	3.9x 10 <sup>-2</sup>	$3.9x$ $10^{-2}$	.5.2x 10 <sup>-2</sup>	4.9x 10 <sup>-2</sup>	3.9x .5.2x 4.9x 5.1x $2.0x$ 1.6x $10^{-2}$ $10^{-2}$ $10^{-2}$ $10^{-2}$ $10^{-1}$ .	2.0x 10 <sup>-1</sup>	1.6x 10-1	2.5x 10 <sup>-1</sup>	2.8x 10 <sup>-1</sup>	1.2x 10 <sup>-1</sup>	8.2x	6.3x	8.0x
Shielding effect in electrical field	67.2 7	70.1	70.3 70.4		71.2	69,9	70.2	69.9 70.2 68.8 51.3 53.2 49.1	51.3	53.2	49.1		46.2 56.0 6.2 9.5	6.2	9.5	6.3
of 300 MHz (dB) *2	68.5 72.1 72.2 72.3 72.3 70.8 71.0 69.8 52.4 55.5 52.3 49.3 59.0 19.3 23.7 18.2	72.1	72.2	72.3	72.3	70.8	71.0	8.69	52.4	55,5	52.3	49.3	59.0	19.3	23.7	18.2

\*1: Carbon black with DBP oil absorption amount of 325 ml/100 g is Ketjen Black BC

Volume resistivity value and shielding effect at electrical field of 300 MHz was measured with 3 samples prepared with the same composition, and the upper limit value and limit value measured are shown. \*2:

#### Example 2

A polypropylene resin (produced by Idemitsu Sekiyu Kagaku, trade name: J-465H) was formulated with the carbon black and various kinds of graphite shown in Table 2 so that the molded plate exhibited a VR of about 1 x  $10^{-1}~\Omega$  cm, and kneaded and molded according to the same method as described in Example 1. The VR, Izod impact strength and specific gravity of the molded plate obtained were measured, and the results are shown in Table 2 in relation to each electroconductive resin composition.

From Table 2 it can be seen that, by using the carbon black and graphite of the present invention, when a VR of about 1 x 10<sup>-1</sup> is exhibited, the filling amount may be about 60% by weight, compared with that when employing a carbon black and graphite other than that of the present invention, whereby the Izod impact strength can be improved and the specific gravity reduced.

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		Present	Present Invention			Comparative	a)
Experiment No.	1.7	18	19	20	21	22	23
Electroconductive resin composition (wt.parts)							
Polypropylene resin	65	<i>L</i> 9	11	70	52.4	53.3	58.7
Oil absorption amount 480 ml/100 g carbon black	10.5	6	8.7	9.0	14.3	14.0	0
" 325 m1/100 g "	0	0	0	0	0	0	12.4
Graphite powder (particle size) Expanded graphite (4.2 µm)	0	. 0	0	0	33.3	0	0
н (40 рм)	24.5	0	0	0		0	28.9
(mt 07)	0	23.1	o	0	0	0	0
(mų 005)	0	0	20.3	0	0	0	
(5 mm)	0	0	0	21.0	0	0	0
Scale graphite (40 µm)	0	0	0	o	0	32.7	O
Volume resistivity value (0.cm)	9.1x10 <sup>-2</sup>	9.7×10 <sup>-2</sup>	9.8×10 <sup>-2</sup>	9.9x10 <sup>-2</sup>	9.5x10 <sup>-2</sup>	9.7x10 <sup>-2</sup>	1.1x10 <sup>-1</sup>
Izod impact strength (kg.cm/cm)	3.0	3.3	4.2	4.2	0.2	0.1	1.1
Specific gravity	1.14	1.12	1.10	1.09	1.25	1.25	1.20
Total amount of carbon black and graphite based on 100 parts by weight of polypropylene	53.8	49.3	40.8	42.9	90.8	97.6	70.2

## Example 3

the weight amount of a high density polyethylene resin (produced by Idemitsu Sekiyu Nagaku,
A 100 parts by weight amount of a high density polyethylene resin (produced by idemitsu Sekiyu Kagaku, and a 100 parts by weight amount of a carbon black with a DBP oil ade name: 520 B) was formulated respectively with predetermined amounts of a carbon black with a DBP oil.
ade name: 520 B) was formulated respectively with predetermined amounts of a state of 500 cm trooped of
osorption amount of 400 mile foo guita tracks and process molded according to the same method as in Example
osorption amount of 480 mi/ 100 g and an expanded graphile with a mount of the same method as in Example of a Laboplastomill at a temperature of 180°C, and press the of the molded plate obtained were measured, and
- up at - history officer and the IZON IMPRO STEPHOLITON LITE HOLDER Plate Obtained in the IZON IMPROCESTED
e results are shown in Table 3 in relation to each electroconductive resin composition.
e results are shown in Table 3 in relation to each electroconductive room and a

Table 3

	•	Present	Present Invention			Comparative	e	
Experiment No.	24	25	26	27	28	29	30	31
Electroconductive resin composition (wt.parts)		-						
High density polyethylene resin	100	100	100	100	100	100	100	100
DBP oil absorption amount 480 ml/100 g carbon black (A)	12.0	10.8	15	13	14.7	7.8	7.5	16
Expanded graphite (average particle size 500 µm) (B)	8.0	7.2	135	711	6.3	5.2	142.5	144
Carbon black A/Expanded graphite (500 µm) B	60/40	60/40	. 10/90	10/90	70/30	60/40	5/95	10/90
Volume resistivity value (0.cm)	2.0x10 <sup>-1</sup>	9.0x10 <sup>-1</sup>	3.5x10 <sup>-2</sup>	4.2×10 <sup>-2</sup>	2.3×10 <sup>-1</sup>	8.0x10 <sup>0</sup>	6.3×10 <sup>0</sup>	*
Shielding effect in electrical field of 300 Miz (dB)	50.6	31.1	72.2	71.4	49.9	رن و.	9.5	* ! .
Izod impact strength (kg.am/am)	3.0	8.2	1.5	2.0	0.2	10.5	1.0	4E 

No sample preparation possible because kneading was impossible.

### Example 4

20 parts by weight). 9 parts by weight of a carbon black with a UBP oil apsorption
Different kinds of resins (70 parts by weight), 9 parts by weight of a carbon black with a UBP oil apsorbidge.
Different kinds of resins (70 parts by weight), 3 parts by weight of an expanded graphite with an average particle size of 500 μm amount of 480 ml/100 g and 21 parts by weight of an expanded graphite with an average particle size of 500 μm
emount of 480 ml/100 g and 21 parts by weight of an expanded graphic through the second second residual to a sequence having a were kneaded and press molded at a temperature shown in Table 4, to obtain a plate 15 cm square having a were kneaded plate were measured, and the kinds of resins, thickness of 2 mm. The VR and the shielding effect of the molded plate were measured, and the kinds of resins, thickness of 2 mm. The VR and the shielding effect of the molded plate were measured, and the kinds of resins, the content of the molded plate were measured, and the kinds of resins, the content of the molded plate were measured, and the kinds of resins, the content of the molded plate were measured, and the kinds of resins, the content of the molded plate were measured, and the kinds of resins, the content of the molded plate were measured, and the kinds of resins, the content of the molded plate were measured.
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thickness of 2 mm. The VH and the shielding effect of the measurement results, are shown in Table 4.
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Table (

Experi-			Molding temperature	Volume resistivity	Shielding effect in electrical
ment No	(kind)	(°C)	(၁°)	value (n·cm)	field of 300 MIz
32	ABS (Mitsubishi Monsanto Kasei, trade name: Tuflex 710)	200	220	2.3 x 10 <sup>-1</sup>	48.9
33	Polystyrene (produced by Idemitsu Sekiyu Kagaku, trade name: SEHI 110)	200 · sku, trade	220	$9.2 \times 10^{-2}$	60.0
34	Polybutyleneterephthalate (Toray, trade name: PBT-1400L)	230	260	$2.2 \times 10^{-1}$	49,4
35.	Polyphenylene oxide (Produced by Engineering Plastic trade name: Noryl 731J-802)	200	220	2.4 × 10 <sup>-1</sup>	48.4
36	Nylon (Produced by Du Pont, trade name: Zaitel ST801)	. 250	270	2.0 × 10 <sup>-1</sup>	50.1
37	Low density polyethylene (Produced by Mitsubishi Yuka, trade name: Yukalon 2F-30)	120	150	9.5 × 10 <sup>-2</sup>	59.6

## Example 5

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A 70 parts by weight amount of a polypropylene resin (produced by Idemitsu Sekiyu Kagaku, trade name:
A 70 parts by weight amount of a polypropheno room (property of 480 ml/100 g and 21 parts by 465H), 9 parts by weight of a carbon black with a DBP oil absorption amount of 480 ml/100 g and 21 parts by
465H), 9 parts by weight of a carbon black with a publish along of 500 um were added with additives for resins
-465H), 9 parts by weight of a carbon black with a bold of size of 500 μm were added with additives for resins veight of an expanded graphite with an average particle size of 500 μm were added with additives for resins
veight of an expanded graphite with all average parties of the expanded graphite with all average parties of an expanded graphite gr
n Table 5, and kneaded and moded according to the same the kinds and amounts of the additives for resins effect of the molded products obtained were measured, and the kinds and amounts of the additives for resins
emeloyed, and the measurement results, are shown in Table 5.
employed and the measurement results, are shown in rable of

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Experiment No.	38	39	40	41	42	43	44
Additives for resins			Amount	Amount added (wt.parts)	.parts)		
Pentaerythrityl-tetrakis 3-(3,5-di- tert-butyl-4-hydroxyphenyl)propiolate	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Phenylsalicylate	0.1	0	0	0.1	0	0.1	0
2-ilydroxy-4-n-octoxybenzophenone	۲.0	0.2	0	0	0	0	0
Trichloroethyl phosphate	0	0	0.1	0.1	0	0	0
Antimony trioxide	5.0		0	5.0	0	0	0
Decabromodiphenyl oxide	0	0	5.0	5.0		0	0
Zinc stearate	0.5	0.5	0	0	2.0	0	2.0
Ethylene bisstearoamide	0	0	0.5	0	0	0.5	. 0
Glass fiber	0	15		0	15	15	0
Volume resistivity value (n.cm)	9.9×10 <sup>-2</sup>	1.3x10 <sup>-1</sup>	9.9×10 <sup>-2</sup>	1.2x10 <sup>-1</sup>	1.3x10 <sup>-1</sup>	1.2×10 <sup>-1</sup>	9.6x10 <sup>-2</sup>
', Shielding effect in electrical field of 300 MHz (dB)	59.1	55.7	59.2	56.8	55.8	56.8	59.5

## Example 6

A thermoplastic resin, carbon black having a DBP oil absorption amount of 480 ml/100 g, expanded
resint, carbon bladt naving agents, lubricants, and plasticizers listed in graphite, antioxidants for resins, flame retardants, reinforcing agents, lubricants, and plasticizers listed in graphite, antioxidants for resins, flame retardants, reinforcing agents, lubricants, and plasticizers listed in graphite, antioxidants for resins, flame retardants, reinforcing agents, lubricants, and plasticizers listed in graphite, antioxidants for resins, flame retardants, reinforcing agents, lubricants, and plasticizers listed in graphite.
graphite, antioxidants for resins, name retailed in 5, removed and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and molded in Tables 6 and 7. The mixture was kneaded and mold
Tables 6 and 7 were formulated in an amount shown in Tables 6 and 7. The molded products obtained were
the same manner as in Example 1. The VR and the shielding effect of the molded products obtained were
measured. The results are shown in Tables 6 and 7 in relation to the composition of the electroconductive
resin

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			Table 6					
Experiment No.	45	46	47	48	49	50	51	52
Composition of electroconductive	ive resin (	(wt. parts)						
Polypropylene resin A	72.5	0	0	0	0	0	0	0
" B*2	0	72.5	0	0	0	0	0	0
*3	0	0	48	0	0	0	0	48
D.*4	0	0	. 0	48	48	36	36	0
ហ្គ * មា , =	<b>o</b>	0	0	0	0	12	12	. 0
Ethylene-propylene rubber A*6	0	0	10	10	0	10	0	0
" B*7	<b>0</b>	0	. 0	0	10	0	.10	. 10
Carbon black having DBP oil absorption amount of 480 ml/100 g	11	11.	11	11	11	11	11	C)
Expanded graphite having particle size 5 mm	16.5	16.5	16.5	. 16.5	16.5	16.5	16.5	27
Talc	0	0	14.5	14.5	14.5	0	0	
Glass fiber	0	0	. 0	0	0	14.5	0	14.5
Calcium carbonate	o ·	0	0	0	0	O	14.5	0
	_							

tinued)	
(Conti	
]e 6	-
Tab Tab	

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Experiment No.	45	46	47	48	49	50	51	52
composition of electroconductive resin (wt. parts)	tive resin (w	. parts)						
Antioxidant for resin A	-	г <del>-</del> і	0	. 0		0	0	0
6* ¤ =	0	0	H	H	<b>-</b> -1	<b>~</b>	Н	H
Ethylenebis hydrogenated	н	r-l	rd į	႕	٦	H	н	٦
tallow acid amide Volume resistivity value (A.cm)	1.1x10 <sup>-1</sup>	1.0x10 <sup>-1</sup>	1.2x10 <sup>-1</sup>	1x10 <sup>-1</sup> 1.0x10 <sup>-1</sup> 1.2x10 <sup>-1</sup> 1.2x10 <sup>-1</sup>	1.0x10 <sup>-1</sup>	1.0x10 <sup>-1</sup> 1.2x10 <sup>-1</sup> 1.2x10 <sup>-1</sup> 1.0x10 <sup>-1</sup>	1.2x10 <sup>-1</sup>	1.0×10 <sup>-1</sup>
Shielding effect in electrical field of 300 MHz (dB)	cal 57.3	58.8	56.4	56.0	57.5	56.2	56.1	57.3

J-5050H Ј-3066н J-465H EP-07P \*3: Idemitsu Petrochemical Co. Japan Synthetic Rubber Co. 4560GE 4200G Karupu Kogyo K.K. \*6: \*4: .. W \*2

Pentaerythtyl-tetrakis 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate Pentaerythtyl-tetrakis 3-(3,5-di-t-butyl-4-hydroxyphenyl)propiolate .. 89 \*

EP-912P

Tris(2,4-di-t-butylphenyl)phosphite = 50/50

\*9:

\*7:

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Experiment No.	53	54	55	26	57	58	59	. 09	61	62
Composition of Electroconductive resin (	(wt. parts	(8)								
6-Nylon resin A	47	0	0	45	0	0	0	0	0	0
" B*2	0	47	. 30	0	0	0	0	0	0	0
c*3		0	20	0	0	0	0	0	0	0
*4 High-density polyethylene resin	0	0	0	0	64	48	0	0	0	0
ABS resin	0	0	0	0	0	0	75	72.5	0	0
PBT resin*6	0	ò	0	0	0	0	0	0	47	20
Carbon black having DBP oil absorption amount of 480 ml/100 g	6.9	6.9	7.5	10	10.8	11	. 10	8.25	6.9	10
Expanded graphite having average particle size of 5mm	16.1 of 5 n	16.1 mm	17.5	15	25.2	16.5	15	19.25	16.1	15
Butyl benzyl phthalate	0	0	0	0	0	0	ហ	0	0	0
Antioxidant for resin A	0	0	0	٦	0	0	0	0	, ,	ᆏ.
. B*8	0	0	0	0	įط	н	Ħ	Н	.0	0
Cuprous iodide	rH	Н	<b>⊢</b> 1	0	0 .	0	0	<b>o</b> .		0

Table 7 (Continued)

Experiment No.	. 53	54	55	56	57	58	59	09	61	62
Camposition of Electroconductive resin (	(wt. parts	(6								
*9 Ethylene-propylene rubber A	0	0	0	0	0	10	0	0	0	0
" *10	0		0	ហ	0	0	0	0	0	.01
Antimony trioxide	3.75	3.75	2.5	3.75	0	0	0	0	3.75	0
Decabromo diphenyl ether	11.25	11,25	7.5	11.25	0	0	0	0	11.25	0
Glass fiber	. 15	15	1.5	10	0	0	0	0	15	1,5
Talc	0	0	0	0	0	14.5	0	0	. 0	0
Ethylenebis hydrogenated tallow acid amide	<b>~</b>	Н	ч	0	Н	H	Н	٦	٦	٦
Benzene sulfonic acid butyl amide	0	0	0	႕	0	0	0	0	.0	0
Volume resistivity value (0.cm)	1.2 x10 <sup>-1</sup>	1.2 ×10 <sup>-1</sup>	1.0 x10 <sup>-1</sup>	1.0 .x10 <sup>-1</sup>	8.3 x10 <sup>-2</sup>	1.3 x10 <sup>-1</sup>	1.0 x10-1	1.0 x10-1	1.1 ×10 <sup>-</sup> 1	1.3 x10 <sup>-1</sup>
Shielding effect in electrical field of 300 MHz (dB)	56.0	56.5	58,3	58.1	61.3	54.0	57.3	57.5	57.1	54.3

Mitsubishi Chemical Co., 1007J (pellet) \*1: , 1007J (Crushed powder \*2: having a size of  $100 - 200 \mu m$ ) 5 Mitsubishi Chemical Co., ST-145 \*3: Idemitsu Petrochemical Co., 110J \*4: Japan Synthetic Rubber Co., JSR ABS 35 \*5: 10 Toray Co., PBT-1400L \*6: N, N'-Hexamethylenebis (3,5-di-t-butyl-4-\*7: hydroxy-hydrocinnamide)/tris(2,4-di-t-butyl-15 phenyl)phosphite = 50/50 Pentaerythtyl-tetrakis 3-(3,5-di-t-butyl-4-\*8: hydroxyphenyl)propiolate 20 Japan Synthetic Rubber Co., EP-07P \*9: T7741P \*10: 25

#### Claims

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1. An electroconductive resin composition comprising (i) 100 parts by weight of at least one resin selected from the group consisting of thermoplastic resins and thermosetting resins and (ii) 15 to 150 parts by weight of (a) carbon black having a DPB oil absorption amount of 400 ml/100 g or more and (b) expanded graphite having an average particle size of 40 µm or more, the expanded graphite content being 40 to 90% by weight of the total amount of the carbon black and the expanded graphite.

2. An electroconductive resin composition as claimed in claim 1, wherein the resin is a thermoplastic

resin.

3. An electroconductive resin composition as claimed in claim 2, wherein the thermoplastic resin is at least one resin selected from the group consisting of low, medium and high density polyethylenes, linear low density polyethylene, polypropylene, ethylene-propylene copolymer, ethylene-vinyl acetate copolymer, ethylene-acrylic acid ester copolymer, acrylonitrile-butadiene-styrene ternary copolymer, polystyrene, acrylonitrile-styrene copolymer, nitrile rubber, butadiene rubber, styrene-butadiene rubber, ethylene-propylene-diene rubber, silicone rubber, thermoplastic polyurethane resin, polyamide resin, polyester resin, polycarbonate, polyvinyl chloride, polyacetal resin, polyphenylene sulfite, and polyphenylene oxide.

4. An electroconductive resin composition as claimed in claim 1, wherein the resin is a thermosetting

5. An electroconductive resin composition as claimed in claim 4, wherein the thermosetting resin is at least one resin selected from the group consisting of thermosetting acrylic resins, phenol resins, unsaturated polyester resins, epoxy resins, urethane resins, and alkyd resins.

6. An electroconductive resin composition as claimed in claim 1, wherein the total amount of the carbon black and the expanded graphite is 20 to 130 parts by weight based on 100 parts by weight of the resin.

7. An electroconductive resin composition as claimed in claim 1, wherein the amount of the graphite is 45% to 85% by weight of the total amount of the carbon black and the graphite.

8. An electroconductive resin composition as claimed in claim 1, wherein the carbon black has a DPB oil absorption amount of 400 to 600 ml/100 g.

9. An electroconductive resin composition as claimed in claim 1, wherein the expanded graphite has an average particle size of 40 to  $20000 \, \mu m$ .

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# EUROPEAN SEARCH REPORT

EP 88 30 5985

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